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(54) HOT MELT ADHESIVE COMPOSITION

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to hot melt adhesive compositions comprising ethylene copolymer suitable for use in making laminated glass windows, especially motor vehicle windscreens.

Laminated glass windows can be made by adhesively bonding together opposed surfaces of opposed sheets of glass by means of a hot melt adhesive composition comprising a copolymer of ethylene, acrylic and/or methacrylic acid and one or more alkyl esters of acrylic and/or methacrylic acid. Such windows have adequate optical properties provided the impurity content of the copolymer is kept reasonably low and provided the temperature to which the copolymer is heated during lamination is carefully controlled. However high levels of impurity in the copolymer and inadequate control of the temperatures at which lamination is carried out can lead to an optical defect in glass laminates made using the copolymer which defect is referred to herein as "blue haze". Blue haze if it is present in a glass laminate can normally be detected by shining a beam of white light through the glass laminate which preferably should be inclined at an angle of 45° to the direction of the beam of light. Under such conditions the laminate will exhibit a hazy pale blue colour if blue haze is present.

By this invention we provide a hot melt adhesive composition comprising an ethylene copolymer and from 0.05 to 2.5% by weight (based on the weight of the composition) of an epoxidised oil which is an ester of one or more polyhydric alcohols with one or more unsaturated fatty acids wherein at least 50% by weight (based on the total weight of the acids) is composed of one or more ethylenically unsaturated or polyunsaturated acids containing from 12 to 24 carbon atoms in their molecules and wherein the ethylene copolymer comprises from 2 to 10 mole % of copolymerised acrylic and/or methacrylic acid and in addition at least some copolymerised acrylic and/or methacrylic ester (the esterifying group being alkyl containing from 1 to 4 carbon atoms) and/or vinyl acetate there being sufficient ester such that the ester and the acid together constitute at least 4 mole % and not more than 14 mole % of the copolymer. It has been found that the use of hot melt adhesives comprising epoxidised fatty acid oils allows larger amounts of impurities to be tolerated in the ethylene copolymers and less stringent control of the temperatures used in making the laminated glass windows, especially motor vehicle windscreens.

The oils which when epoxidised are most useful in the performance of this invention are the glycerides of unsaturated fatty acids which occur in vegetable oils such as corn oil, cottonseed oil, hempseed oil, linseed oil, peanut oil, olive oil, palm oil, sesame oil, poppyseed oil and sunflowerseed oil. However the preferred oil is soybean oil. Epoxidised fish oils may also be useful. The epoxidisation of the polyesters may be carried out by any standard process such as those described on pages 253 to 256 of volume 8 of the second edition of "The Encyclopedia of Chemical Technology" edited by R. E. Kirk and D. F. Othmer and published by Interscience. Preferably the epoxidised oils used in the performance of this invention should have a molecular weight of from 800 to 1,200. Examples of commercially available epoxidised oils include "Harflex" 2020 (Wallace and Tiernan Inc) and "Paraplex" GG2 (Rohm and Haas Company) and "Estabex" 2307 (Akzo). "Harflex" and "Paraplex" are registered Trade Marks.

The ethylene copolymer used in the performance of this invention preferably comprises methacrylic acid and either a methacrylate (especially methyl mathacrylate) or an acrylate (particularly butyl acrylate). The preferred ethylene copolymer comprises from 2.65 to 7.75 mole % of copolymerised acrylic and or methacrylic acid and copolymers comprising

3.85 to 6.10 mole % of acid are particularly preferred. Preferably the ethylene copolymer has a melt flow index of from 0.1 to 5 (as measured according to British Standard 2782: Part 1 1956 Method 105C: Procedure A) but the most preferred melt flow indices lie in the range 0.1 to 2.0 and especially in the range 0.5 to 1.2.

The ethylene copolymers may be prepared by the known process of ethylene polymerisation at high pressure, the mixture of comonomers being polymerised at a pressure above 100 MN/m^2 (1000 atmospheres), in the presence of a free radical polymerisation initiator, and at elevated temperature, suitably 120° C to 250° C. The monomers are introduced in the proportions found to give the desired proportions in the copolymer under the conditions of the reaction. To make copolymers of the highest transparency it is preferred that a well-stirred continuous autoclave reactor be used.

The hot melt adhesive compositions of this invention may be conveniently converted into foils of from 0.35 mm to 1.15 mm in thickness. The foils may be employed in a widely used process for the production of laminated glass windows (especially motor vehicle windscreens) in which sheets of glass with the foil of hot melt adhesive composition sandwiched between them are assembled in a suitable jig, and the assembly is placed in a flexible bag of plastics or rubber. The bag is then thoroughly evacuated, and the sandwich is placed in an oven, or in an air- or oil-heated autoclave, and heated to a temperature above the softening point of the adhesive. For the hot melt adhesive compositions employed in making windscreens according to the present invention this temperature is generally above 110° C (for example between 110° C and 160° C) and heating is carried out for a period of about 15 to 30 minutes. However, different temperatures and different time cycles may be used. The pressure of the atmosphere (when an oven is used) or the pressure applied in an autoclave, provides for uniform contact and bonding between the curved sheets of glass and the hot melt adhesive composition. Often the sandwich is removed from the bag and subjected to further heating at temperatures of from 110° C to 160° C). The assembly is then cooled or allowed to cool.

To obtain maximum transparency of the hot melt adhesive composition, the sandwich is preferably cooled as rapidly as is possible without risk of causing breakage of the glass. Alternatively, if it is more convenient to allow the sandwich to cool slowly, full transparency may be restored by reheating the sandwich to a temperature of about 100° C and then rapidly cooling it. In either case, the sandwiches may be cooled by plunging them into liquid cooling medium, usually water, suitably at about 40° C to 65° C. Cooling may alternatively be accomplished by means of blasts of cold air or water.

The glass surfaces to be bonded may if desired be treated with an adhesion promotor before the sandwich is assembled. For example, silanes of the type described in British patent specification 1,095,700 may be used for this purpose.

By this invention we also provide a laminated glass window (especially a motor vehicle windscreen) comprising opposed sheets of glass whose opposed surfaces are adhesively bonded together by means of the hot melt adhesive composition herein disclosed.

The invention is illustrated by the following examples.

EXAMPLE 1.

An ethylene copolymer of melt flow index 0.76 dg/10 min and containing 12.6% by weight of copolymerised methacrylic acid and 13.5 wt % of copolymerised methyl methacrylate was converted into foil of thickness 760 μm. A glass laminate was produced by sandwiching one layer of the foil between two sheets of clear float glass 3 mm thick and heating the sandwich for a total of 40 min at 120° C. During the first 20 minutes of this heating the sandwich was placed under vacuum to remove any air present between the glass and foil. The sandwich was heated for a further 30 minutes at 110° C and then quench-cooled in water whose temperature was 50° C.

The laminate was cut in half and one half was reheated for 1 hour at 160° C, then for 30 minutes at 100° C and was finally quenched in water at 50° C as previously. The two halves were removed to a darkened room and examined for blue haze by being placed in the beam of light from a 1000—W tungsten filament projector bulb. The half that had been heated for 1 hour at 160° C was found to show a marked bluish haze due to side-scattering of the light passing through the laminate. The half that had not been reheated to 160° C showed little or no blue haze in comparison.

EXAMPLE 2.

Laminates were made as described in Example 1 using a foil produced from a copolymer which was the same as that described in Example 1 except that it additionally contained various concentrations (as set out in Table 1) of 'Paraplex G62' which is an epoxidised soybean oil sold by Rohm and Haas Co. As in Example 1, one half of each specimen was heated to 160° C for 1 hour, and quench-cooled from 100° C to 50° C.

The laminates were examined for blue haze as in Example 1 and were found to show effects described in Table 1.

TABLE 1

Sample	Concentration of epoxidised soybean oil wt %	Appearance:	
		as laminated at 120°C and quench-cooled	after heating 1 hr at 160°C and quench-cooling
A	0	clear, no blue haze	marked blue haze
B	0.125	clear, no blue haze	slight blue haze, better than A
C	0.25	clear, no blue haze	very slight haze, better than B
D	0.50	clear, no blue haze	better than C
E	1.0	clear, no blue haze	no blue haze
F	2.0	clear, no blue haze	no blue haze

EXAMPLE 3.

By a process similar to that described in Example 1, a glass laminate was made using a foil of the ethylene copolymer described in Example 1 except that the copolymer also contained 1 wt % of a non-epoxidised cottonseed oil. One half of the laminate was reheated to 160° C for 1 hour, quenched and re-examined. The laminates were examined for blue haze as in Example 1 and the results are set out in Table 2.

TABLE 2

Sample	Concentration of cottonseed oil wt %	Appearance:	
		as laminated at 120°C and quenched	after heating 1 hr at 160°C and quenching
G	0	clear	blue haze
H	1	clear	blue haze

Table 2 indicates that the use of a non-epoxidised vegetable oil does not help in reducing blue haze.

EXAMPLE 4.

Laminates were made as described in Example 1 using a foil produced from the ethylene copolymer described in Example 1 except that the copolymer also contained various concentrations of epoxidised soybean oil as set out in Table 3. The lamination temperature cycle was modified so that each laminate was heated at 120° C for 30 minutes under vacuum then for 45 minutes at 160° C and 15 minutes at 100° C before being finally quench-cooled in water at 50° C.

The laminates were examined for blue haze as in Example 1 and found to show the following effects as set out in Table 3.

TABLE 3

Sample	Concentration of epoxidised soybean oil wt %	Appearance
I	0	marked blue haze
J	.125	slight blue haze
K	.25	slight blue haze
L	.5	no blue haze
M	1	no blue haze

EXAMPLE 5.

Using a process similar to that described in Example 1, a glass laminate was made using foil produced from the polymer described in Example 1. The foil was incorporated into the laminate in the form of parallel bands of foil one of which consisted of polymer containing no additive, while the other bands consisted of polymer containing, respectively, 0.125, 0.25 0.5, 1.0 and 2.0 wt % of 'Lankroflex L', an epoxidised linseed oil (Lankro Chemicals Ltd). The laminate was cut in half along a line bisecting each of the parallel bands of foil. One half of the laminate was reheated for 1 hour to 160° C, then quenched and re-examined for blue haze as described in Example 1. The effects found are set out in Table 4.

TABLE 4

Concentration of epoxidised linseed oil wt %	Laminate half as made	Laminate half reheated 1 h at 160°
0	clear, no blue haze	marked blue haze
0.125	clear, no blue haze	slight blue haze
0.25	clear, no blue haze	very slight blue haze
0.5	clear, no blue haze	no blue haze
1.0	clear, no blue haze	no blue haze
2.0	clear, no blue haze	no blue haze

WHAT WE CLAIM IS:—

1. A hot melt adhesive composition comprising an ethylene copolymer and from 0.05 to 2.5% by weight (based on the weight of the composition) of an epoxidised oil which is an ester of one or more polyhydric alcohols with one or more unsaturated fatty acids wherein at least 50% by weight based on the total weight of the acids) is composed of one or more ethylenically unsaturated or polyunsaturated acids containing from 12 to 24 carbon atoms in their molecules and wherein the ethylene copolymer comprises from 2 to 10 mole % of copolymerised acrylic and/or methacrylic acid and in addition at least some copolymerised acrylic and/or methacrylic ester (the esterifying group being alkyl containing from 1 to 4 carbon atoms) and/or vinyl acetate there being sufficient ester such that the ester and the acid together constitute at least 4 mole % and not more than 14 mole % of the copolymer.

2. A composition according to Claim 1 wherein the epoxidised oil comprises the epoxidised polyhydric alcohol ester of a vegetable oil.

3. A composition according to Claim 2 wherein the polyhydric alcohol ester is a glyceride.

4. A hot melt adhesive composition compris-

ing a copolymer of ethylene with acrylic and/or methacrylic acid and an acrylate and/or methacrylate and an epoxidised ester of a vegetable oil substantially as hereinbefore described and illustrated by means of the non-comparative parts of Examples 2, 4 and 5.

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